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Some Properties of Gamma-Irradiated Starches and Their Electrodialytic Separation

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In a series of former contributions we demonstrated that starch is very sensitive towards different forms of irradiation.[1-3] Potato starch yields a nice form of soluble starch, which is not only of theoretical interest but also well suited for applications in the paper industry and textile fabrication.

Recently we extended our experiments to wheat and maize starch. The wheat starch was especially interesting, as observations made in our institute[4,5] showed that the baking quality of wheat flour improved after irradiation.

Many properties were used in characterizing such products. In this paper we refer to observations with solutions of starch which received a dose of 2,000,000 rep.

This dose which alters potato starch to a typical soluble form was expected to produce different changes in the wheat and maize starches because of their different constitutions as cereal starches.

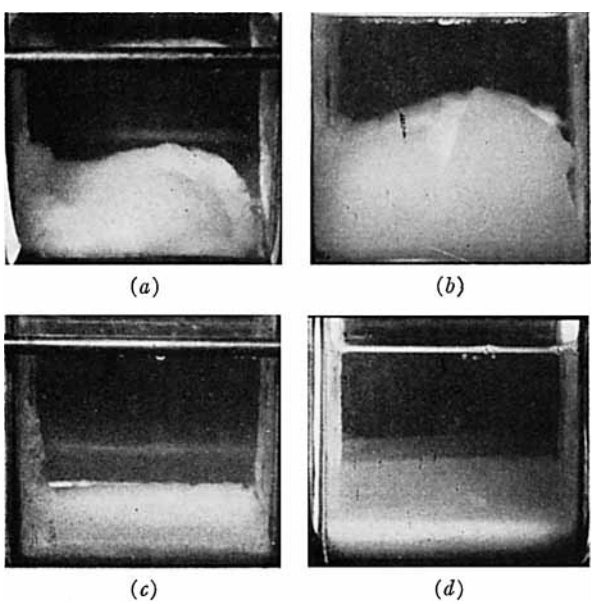

Fig. 1. Separation of (*a*) unirradiated wheat starch; (*b*) unirradiated maize starch; (*c*) irradiated wheat starch; (*d*) irradiated maize starch.

Potato, wheat, and maize starches in the form of air-dried solids were exposed to gamma rays (of Co^{60}) in glass vessels. We investigated the starches at a concentration of about 2%, in the state of a paste and as a solution prepared by heating for 30 min. at 120°C.

Electrodialysis separates solutions of potato starch into two phases, which would correspond to the amyloses and the amylopectins, respectively, if the solutions had not been heated too long. The same separation occurs when wheat and maize starch are treated in the same manner. Figure 1 shows such a separation for solutions of irradiated and unirradiated samples of wheat and maize starch. As can be seen, there results also with unirradiated samples some quantity of a clear sol substance which corresponds in general to a solution of amylose. At higher irradiation doses the separation of the phases becomes easier and more complete.

In the discussion we shall not refer to the "pure" amyloses and the "pure" amylopectin but only to a sol phase and a gel phase. The degree of the separation of the sol depends upon the nature of starch. Some data are given in Table I as the concentrations of gels. It is evident that the irradiated starches have undergone a more complete separation than the unirradiated ones. The data show that the potato starch is much more sensitive to gamma rays than the two other kinds. Already at 100° there results an almost clear, thin-flowing solution.

In the three starches the gamma rays cause the following changes of properties: (*a*) the viscosity decreases; (*b*) the reducing power increases a little; (*c*) the binding of iodine decreases a little; (*d*) the splitting off with β-amylase becomes smaller. The influence of the rays upon the size of particles is very varied.

TABLE I
Some Properties of Unirradiated Starches and Starches Irradiated with 2,000,000 Rep[a]

	Potato		Wheat		Maize	
	Untreated	Irradiated	Untreated	Irradiated	Untreated	Irradiated
Appearance	Pasty, opaque	Almost clear	Very turbid	Turbid	Turbid	Turbid, jellylike
Relative viscosity	1.63	1.12	1.16	1.07	2.50	1.15
Reducing power	0.94	1.55	0.90	3.54	0.44	2.34
pH	6.00	6.30	6.00	4.25	6.00	4.25
Iodine absorption	4.40	3.70	3.10	3.00	3.26	3.70
% split off with β-amylase	69.00	62.00	68.00	67.60	68.00	
Molecular weight	148,241	57,336	164,000	264,431	389,000	236,517
% coagulated	0	0	0	13		
Portion permeable through collodium, %	1.00	8.90	3.00	33.00	5.20	24.60
Electrodialytically inseparable	27.10	50.80	57.20	69.20	19.30	48.40
Sol pH	4.40	4.50	5.00	5.50		5.10
Iodine absorption of sol, %	16.20	11.00	4.73	3.80	13.60	5.46
P_2O_5 in sol, %	0.027	0.031	0.022	0.028	0	trace
Gel concentration, %			5.50	9.90	4.80	7.30
Gel pH	2.90	2.90	3.90	3.40	4.40	3.50
Iodine absorption of the gel, %	3.50	1.18	2.80	3.80	1.70	4.20
P_2O_5 in gel, %	0.135	0.094	0.187	0.221	0.053	0.078

[a] Solutions (approx. 2%) seated 1/2 hr. at 120°C.

The osmotic molecular weight increases in potato-starch. In the same way, the portion of the substance which penetrates through a permeable collodium increases as a result of the decreased particle size.

Wheat and potato starch yield quite a different picture after the osmosis has taken place. With wheat starch there is an extraordinary increase in the size of particles. Part of the substance coagulates during the determination of the osmotic pressure and may be centrifugated off. The molecules of a third portion (about a third of the sample) became so small that they could penetrate through the membrane. As in the beginning, the osmotic pressure in the solutions of wheat starch increases very quickly, then decreases, and finally falls to a constant value. We may suppose that these solutions are very heterodisperse. With unirradiated wheat starch the more finely dispersed portion has the higher osmotic pressure. With irradiated starch a part is broken down to a form which cannot pass through the membrane. Therefore the osmotic pressure decreases and the molecular weight increases. The effective coagulation of a part of the substance during osmometry may indicate certain resynthetic processes which we assume exist also with potato starch.

Large differences exist in the behavior on electrodialysis. In our three-cell apparatus (Fig. 1), all three starch solutions separate, but the proportion of electrodialytically unseparable material varies widely. This portion is relatively small with potato starch (27.1%); with wheat starch it is about 57%, and with maize starch, about 19.3%. Irradiation causes an increase in the relative quantity of the sol in all samples, especially with maize starch.

The iodine color of these clear sols is pure blue and changes to green with an excess of iodine, a typical reaction of the "amylo" substances. The iodine-binding power is extremely different. The sol of potato starch binds 16.2% iodine. The sol of potato starch from gelatinized starch which was not heated under pressure binds almost 20% of iodine, which value is near the limiting value of 21.6% iodine given by Higginbotham.[6]

In contrast, the sol substance of the wheat starch binds only 5.5%, and the sol substance of maize starch, 13.6%.

Assuming that the iodine-binding power characterizes the unbranched structure which tends to form spirals, we must suppose that the substance in the sol corresponding to the amylose consists of branched molecules, an assumption that should be verified by organic chemical investigations.

Solutions of wheat and maize starch prepared under pressure are somewhat acid, while the solutions of potato starch are almost neutral (pH = 6).

After irradiation, maize starch becomes acid, while the pH is unchanged with the two other starches.

After electrodialysis the gel phase is much more acid than the sol phase and even more acid than the original solution. Though some observations after high irradiation doses indicate some oxidation, it seems to be the organically bound phosphoric acid which represents the principal cause of acidification and can be determined analytically after extreme electrodialysis in the gels and (with exception of the maize starch) also in the sols. Only small quantities of the organically bound phosphorus are split off by irradiation.

In general, irradiation produces degradative changes in starch which leads to soluble starches fit for technical use.

References

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Summary

Potato, wheat, and maize starches were irradiated in glass vessels with a dose of 2,000,000 rep of gamma rays from Co^{60}. The starches were heated for 30 min. at 120° and their solutions were investigated. In general, there occurs a change of the starch into soluble starch. The viscosity of the three starches in solution decreases, the reducing power increases a little, the iodine-binding power and the splitting off with β-amylase decrease. With potato starch, the macromolecules become somewhat smaller, as determined by osmometric investigation; with cereal starches the molecules are mostly degraded into smaller particles. The solutions of all three starches can be fractionated by electrodialysis. After irradiation the portion in colloidal solution increases.

Résumé

Les amidons de pomme de terre, de froment et de mais ont été irradiés dans des tubes de verre avec une dose de 2.000.-000 rep au moyen des rayons gamma. Comme source des rayons, le Co^{60} à 308 cu fut choisi. Les amidons furent chauffés, 1/2 h. à 120° et leurs solutions examinées. On observe en général une transformation de l'amidon en amidon soluble. Pour tous les trois amidons, la viscosité diminue, le pouvoir réducteur augmente faiblement, le pouvoir d'absorbtion d'iode diminue, de même que la dégradation par la amylase. L'osmométrie indique une dégradation partielle des macromolécules dans le cas de l'amidon de pomme de terre, tandis que pour les amidons de céréales une importante dégradation des molécules en molécules plus petites est observée. Les solutions des trois espèces d'amidon peuvent être fractionées par séparation électrodialytique; par irradiation, la partie colloidale soluble augmente.

Zusammenfassung

Kartoffel-, Weizen- und Maisstärke wurden in Glasgefässen mit Gammastrahlen der Dosis 2.000.000 rep bestrahlt. Als Strahlenquelle diente ^{60}Co von 308 Curie. Die Stärkeproben wurden 1/2 Stunde lang bei 120° gelöst und diese Lösungen untersucht. Im allgemeinen beobachtet man eine Veränderung der Stärke im Sinne der Bildung löslicher Stärke. Bei allen drei Stärkearten nimmt die Viskosität der Lösungen ab, das Reduktionsvermögen steigt ein wenig an und das Bindungsvermögen für Jod, ebenso wie die Spaltbarkeit durch β-Amylase nimmt ab. Bei der Kartoffelstärke lassen die osmotischen Messungen einen teilweisen Abbau der Makromoleküle erkennen, bei den Getreidestärken kommt es zu einer starken Zertrümmerung der Moleküle in kleine Teilchen. Die Lösungen aller drei Stärken lassen sich elektrodialytisch zerlegen; durch die Bestrahlung wächst der kolloid-lösliche Anteil an.

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